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PYROMETALLURGICAL SLAGS AS A POTENTIAL SOURCE OF SELECTED METALS RECOVERY

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Complex analysis of concentration and form of occurrence such metals as Zn, Pb, Fe and Cu in slags formed during a current zinc production in the Imperial Smelting Process (ISP) is a possible basis for development of optimal recovery technology. For this purpose studies of slags from the current production of the Shaft Furnace Unit and of the Lead Refining of the "Miasteczko Śląskie" Zinc Smelting Plant were carried out. The studies results show that slags includes high concentrations of: Zn from 0,064 % to 1,680 %, Pb from 10,56 % to 50,71 %, Fe from 0,015 % to 2,576 %, Cu from 7,48 % to 64,95 %, and change in a broad range. This slags show significant heterogeneity, caused by intermetallic phases (Zn - Pb, Cu - Zn, Cu - Pb) formed on the surface thereof. It is so possible that slag can be a potential source of this metals recovery.

Key words: slag, zinc smelting plant, shaft furnace unit, lead refining unit, metals

INTRODUCTION

The "Miasteczko Śląskie" Zinc Smelting Plant (HC Miasteczko Śląskie) is the only zinc and lead manufacturer in Poland that uses the ISP pyrometallurgical process. The process line includes a sintering plant, sulphuric acid plant, cadmium plant, shaft furnace and lead refining plant [1, 2]. In addition to the main products (pyrometallurgical zinc, lead bullion, metallic cadmium, sulphuric acid) the process generates a by-product (Zn - Pb sinter) and solid wastes (slags, slurries, dross) [1, 2].

Slags formed in the ISP process are the only waste at HC Miasteczko Śląskie that is disposed at the Hazardous Waste Landfill. All other waste is recycled within the process.

The determination of the amount of heavy metals and of the form of occurrence thereof in the slags currently generated and slags deposited in the landfill, the said determination being already partially done [3, 4], may create a basis for developing an optimized process for the recovery thereof.

To this end preliminary tests were carried out on slags taken from the current zinc production in the ISP process to determine the content of selected heavy metals (i.e. Zn, Pb, Fe, Cu) therein. Preliminary tests of the phase composition of these slags were also conducted.

The Imperial Smelting Process applied at HC Miasteczko Śląskie consists in reducing a roasted concentrate with coke. The characteristic feature of the ISP process is that it produces zinc and lead concomitantly [5].

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The basic manufacturing line at HC Miasteczko Śląskie is concentrated around the shaft furnace and comprises [5]:

– Sintering Unit, which also includes the Sulphuric Acid Plant and the Cadmium Plant,
– Shaft Furnace Unit (reduction of zinc and lead compounds),
– Zinc and Lead Refining Units (pyrometallurgical removal of contaminants from the shaft furnace products).

The Shaft Furnace Unit includes two process lines: furnace charge preparation shop and shaft furnace plant, where zinc compounds are reduced and distilled and lead compounds are reduced at a temperature of 1 000 °C. The products obtained from the shaft furnace are: zinc in vapour form and lead in liquid form. The wastes generated in the process, dross and dust, are transferred back to the Sintering Unit, whereas the slag (shaft furnace slag) is granulated and delivered to the landfill. Ca. 60,000 Mg of slag are retrieved from the shaft furnace process every year [3].

The Lead Refining Unit includes a number of process lines where the following sequential operations are performed: drossing, decoppering, softening, desilverizing, debismuthizing, final refining [5]. The process enables complete refining of lead, i.e. removal of such impurities as Cu, Sn, As, Sb, Ag and Bi. The product is refined lead, whereas the only waste removed and deposited is the slag formed in the Short Rotary Furnace (SRF). Ca. 700 Mg of slag formed in this Unit are deposited every year [5, 6].

SAMPLING AND METHODS

Slags from the current production of the Shaft Furnace Unit and of the Lead Refining Unit were sampled in two series, each of which comprised 8 samples from each unit. In consideration of the homogeneity of the slag samples from the shaft furnace, these samples were averaged and analysed thereafter.

Samples taken from the current production were mineralized and then analysed by atomic absorption spectrometry (AAS) to determine Zn, Pb, Fe and Cu content [7]. addition, slag samples, upon preparing microscopic specimens, were subjected to X-ray microanalysis to determine the phase composition thereof. Phase identification was based on the X-ray diffraction method using an HZG4 diffractometer equipped with a digital data collection interface and $Cu_{K\alpha}$ lamp (voltage 35 kV, current 16 mA) [8].

RESULTS AND DISCUSSION

Zinc content in slag from the Lead Refining Unit varies in a broad range (from 0,064 % (sample 4) to 1,680 % (sample 1) with 1,625 % content in the averaged sample (Table 1), which probably is the result of the formation of intermetallic phases on the surface [9] where the elements determined are concentrated (Figure 1). Shaft furnace slags (sample 10) contain substantial amounts of Zn, i.e. 7,462 %, which may be an indication of incomplete reduction of zinc oxides during the shaft furnace process.

Lead in the slags from the SRF is present in high concentrations varying in a broad range from 9,850 % (sample 6) to 50,710 % (sample 4), with 14,140 % content in the averaged sample (Figure 1). Lead in the samples analysed forms intermetallic compounds (Cu-Pb alloys probably) (Table 1). Lead content in samples from the Shaft Furnace is much lower (3,980 %), which is the result of strong reduction of lead oxides during the shaft furnace process.

Fe content varies in a broad range from 0,015 % (sample 2) to 2,576 % (sample 1), with 2,290 % content in the averaged sample (Figure 1). Iron concentration in the slag from the shaft furnace is higher at 6,410 % (Table 1). As iron is the basic slag-forming constituent, its content is dictated by the requirements of the shaft furnace and lead refining processes.

Copper content shows large variation in samples of slag from the SRF: from 7,480 % (sample 4) to 64,950 % (sample 5), with 23,180 % content in the averaged sample (Figure 1). Copper forms intermetallic phases (Cu-Zn (brass), Cu-Pb alloys probably) on the sample surface (Table 1). Copper content in samples from the shaft furnace is much lower (3,770 %), which is the result of the reduction of copper oxides and transfer of copper to lead bullion.

The analysed slags from the Shaft Furnace Unit, as shown by identification using X-ray diffraction, contain lead mainly in the oxide form, i.e. PbO, while zinc is present in the form of ZnO.

In the slags from the Lead Refining Unit these elements form mainly intermetallic compounds: Zn-Pb, Cu-Zn and Cu-Pb.

Table 1 **Zn, Pb, Fe, Cu content in slag samples taken from current production / wt. %**

Sample no.	Source	Element determined			
		Zn	Pb	Fe	Cu
1	LRU SRF	1,680	11,170	2,576	24,140
2		0,234	43,610	0,015	17,380
3		0,591	10,560	0,420	21,450
4		0,064	50,710	0,037	7,480
5		0,768	31,200	0,596	64,950
6		0,230	9,850	1,235	20,510
7		0,078	11,030	0,614	23,750
8		1,528	12,630	0,068	16,580
9	Averaged sample LRU, SRF	1,625	14,140	2,290	23,180
10	SFU	7,462	3,980	6,410	3,770

Explanation: LRU SRF – Lead Refining Unit, Short Rotary Furnace, SFU - Shaft Furnace Unit.

The prevalent forms of iron occurrence in the slags from the current production are silicates $2FeO{\cdot}SiO_2$ and ferrites $ZnO{\cdot}Fe_2O_3$, with seldom presence of oxide form FeO. Copper is mainly present as an admixture to Zn and Pb oxide forms and also forms alloys with lead and zinc (brass). It should be noted that the elements determined usually form complex multiphase systems, being the result of thermal transformations occurring in the course of the industrial process.

Table 2 **Quantities of metals determined in slags from the current production by the ISP process**

		LRU SRF	SFU	Total
	Slag quantity/ Mg/year	700	60 000	
Element	Zn	11,375	4 477	4 489
	Pb	98,98	2 388	2 487
	Fe	16,03	3 846	3 862
	Cu	162,26	2 262	2 424

Explanation: see Table 1.

The amounts of elements present in slags from the current production in the Lead Refining Unit and the Shaft Furnace Unit were calculated on the basis of the quantity of slags produced annually and the determined content of individual metals in these slags. As shown by these calculations (Table 2), the largest amounts of elements are recoverable from slags from the Shaft Furnace Unit. This is mainly due to the fact that this type of slag is generated in large amounts. Slags from both Units jointly contain the following amounts of elements: nearly 4 500 Mg of Zn and 2 500 Mg of Pb, more than 3 800 Mg of Fe and 2 400 Mg of Cu.

The selection of the best method of the recovery of elements such as Zn, Pb, Fe and Cu depends in the first place on the phase composition of the slags, which may form a source of these metals. This was indicated earlier in the research conducted by [3], although then the tests were performed on slags deposited in the landfill. This landfill may constitute an anthropogenic deposit for these metals.

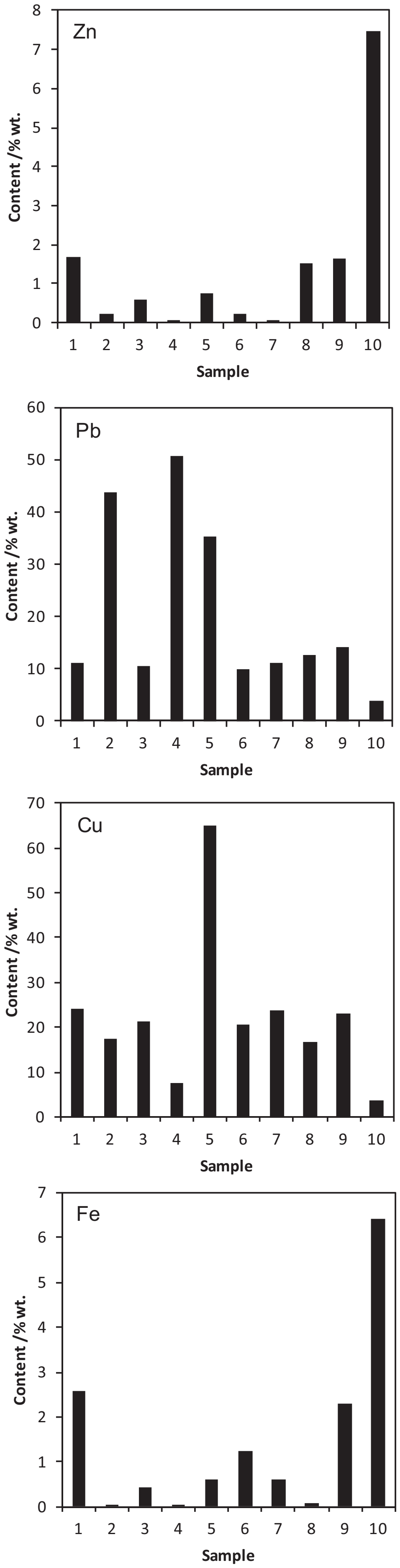

Figure 1 Zn, Pb, Fe and Cu content in slags from current production by the ISP process

As Zn, Pb, Fe and Cu occur in slags from the current production mainly in the form of intermetallic compounds and oxides, these metals may be recovered in the fuming process (metal oxides reduction with carbon monoxide) or the Waelz process (high-temperature reduction of metal compounds). The products obtained in these processes include a metallic/sulphide phase and dust, while the slag formed is glassy in form.

If Zn, Pb, Fe and Cu occur mainly in the form of intermetallic compounds, these metals can then be also recovered from the slag using the conventional or dry Harris process. The conventional process consists in oxidation using sodium nitrate in the presence of sodium hydroxide. The dry method is a modification of the conventional process wherein the amount of sodium hydroxide used is reduced. The process generates metal oxides.

All methods of metal recovery from slags from the current production will contribute to the reduction of slag mass and volume, which is a desirable environmental effect:

– reduction of the quantity (mass and volume) of slags deposited in the environment (landfill),
– limitation of heavy metals migration to the environment by elimination thereof from slags deposited in the landfill,

while at the same time providing an economic justification for the implementation of these methods.

SUMMARY AND CONCLUSIONS

Slags from the current production, derived from the Shaft Furnace Unit and the Lead Refining Unit, vary considerably in the content of elements determined, i.e. Zn, Pb, Cu and Fe. Slags from the current production of the Shaft Furnace Unit are characterized by varying content of heavy metals: 7,462 % Zn, 3,98 % Pb, 6,41 % Fe, 3,77 % Cu.

Slags from the Short Rotary Furnace (Lead Refining Unit) show significant heterogeneity, caused by intermetallic phases (Zn-Pb, Cu-Zn, Cu-Pb) formed on the surface thereof.

Content of the elements determined vary in a broad range: Zn from 0,064% to 1,680%, Pb from 10,56 % to 50,71 %, Fe from 0,015 % to 2,576 %, Cu from 7,48 % to 64,95 %.

As Zn, Pb, Fe and Cu occur in slags from the ISP process mainly in the form of intermetallic compounds and oxides, the suggested methods of metals recovery include the fuming process, the Waelz process and the Harris method.

In addition to providing economic benefits, the development of an optimum process for the recovery of elements present in metallurgical slag will gradually reduce the quantity of waste, the landfilling of which has an adverse environmental effect.

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Note: The responsible translator for English language is J. Olender, Gliwice, Poland